

THE CATALYTIC VAPOR-PHASE PARTIAL OXIDATION OF
CROTONALDEHYDE IN THE PRESENCE OF OXIDES
OF VANADIUM AND MOLYBDENUM

by

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INTRODUCTION

The catalytic partial oxidation of organic compounds in the vapor phase presents remarkable possibilities in the development of modern chemical industry. Unfortunately, however, the theory of catalysis in heterogeneous systems has been developed far beyond the knowledge of its practical application, mainly because the factors which govern these processes are so varied in character and significance that specific agreement among different investigators is seldom, if ever, found.

The excellent pioneering work of Jaeger (5), Weiss and Downs (10), and others on the partial oxidation of benzene, naphthalene, and anthracene has been extended by later investigators into the oxidation of a great many organic compounds belonging to the aliphatic series. But so far, most attention has been paid to compounds of a saturated nature, and the direct oxidation of the olefinic hydrocarbons has not been investigated nearly so extensively as the same reaction of the paraffins (4). This is in keeping with the more restricted supply of olefines, as such, but out of harmony with the greater activity of these compounds.

The value of unsaturated substances when used in simpler and more productive processes has apparently de-

tered extensive research programs on their direct oxidation. But even though practical and economic restrictions at present limit the industrial processing of aliphatic compounds by vapor-phase oxidation to simpler members of the paraffinic series, the olefinic double bond is, nevertheless, rapidly reaching a point of tremendous theoretical significance in catalytic vapor-phase oxidation. The olefin double bond possesses some unique structural or dynamic property by virtue of which it is able to incite chemical reactions which are precisely contrary to well-established principles of behavior concerning certain organic configurations, in particular, the methyl group.

As compared to other organic structures, the methyl group is salient in its indifference to oxidation; when oxidation does take place, it is generally a complete decomposition to carbon dioxide and water. Olefinic compounds, on the other hand, are very readily oxidized. In milder oxidations, two hydroxy groups are added to the molecule, and a dihydric alcohol is formed. In more violent reactions, the olefine molecule is ruptured at the point where the double bond exists, and a mixture of simpler acids and ketones is obtained (1).

The behavior of crotonaldehyde, $\text{CH}_3\text{-CH:CH-CHO}$, is paradoxical in its apparent contradiction to the expected

phenomena. When its vapors are passed with air over certain heated catalysts, the "unstable" double bond remains intact, and the indifferent methyl group oxidizes to a carboxyl group. Thus where a rupture, if not a complete decomposition of the molecule might justly be expected, the thermally stable dicarboxylic compound, maleic acid (HOOC-CH:CH-COOH), is formed (2). Since this phenomenon is not to be found among reactions involving saturated compounds, the double bond must in some way be responsible for this desultory behavior of the methyl group. In the absence of appropriate experimental information, the true significance of the double bond in this type of reaction, is, as yet, obscure; and so it is quite beyond the scope of this work to attempt a final solution of the problem from the standpoint of the double bond. However, the double bond can demonstrate its influence only in the presence of certain catalysts; and, therefore, determining the exact significance of the catalyst in this reaction affords a very strategic point at which to attack the problem.

The very nature of the catalytic oxidation processes and the thermodynamic changes involved suggest that the investigation of a catalytic reaction be conducted with four major objectives in view:

1. The effect of the catalyst itself with respect to its physical and chemical nature.

2. The influence of the reaction temperature.
3. The significance of concentration in the reacting mixture.
4. The importance of the velocity at which the gaseous mixture passes over the catalyst.

APPARATUS AND PROCEDURE

Perhaps the greatest criticism of recent work on vapor-phase oxidation is that each investigator has used an entirely different apparatus in his work, making it impossible to duplicate work done with one apparatus when using an apparatus of a slightly different design. Any attempt to advance the study of vapor-phase oxidation into the realm of the unsaturated compounds should, therefore, be first concerned with the development of a suitable apparatus, especially adapted to handling the reactants and products involved, yet of a simple construction which might be easily reproduced and, by means of which, the work of one investigator might be accurately and conveniently duplicated. The development of just such an apparatus has been a primary purpose of this work. Numerous practical difficulties arising from the use of unsaturated compounds have necessitated many notable departures from the more common types of equipment for this kind of work, but in the end,

an apparatus has been developed which operates very satisfactorily and which might well be used as a prototype for future designs.

Discussion of Method

The apparatus used is shown on Diagram I. Compressed air from a regulating needle-valve passes through a drying tower containing calcium chloride, then through an orifice meter where the rate of flow is measured, and thence into an air receiver equipped with a thermometer and a U-tube manometer for determining the temperature and pressure of the inlet air. In the carburetor, crotonaldehyde is fed into the air at a constant regulated rate from a vertical capillary tube connected to an aldehyde reservoir. A vigorous agitation as the air and aldehyde vapors pass over a baffling of aluminum turnings, combined with heat from an electric resistance coil, insures thorough mixing to a homogeneous gaseous mixture. These vapors then rise through the catalyst where, under the combined effects of catalyst and heat from an electric heater, oxidation occurs. The hot gases, which now contain the reaction products, are then led into a water condenser where most of the solid and liquid material condenses out. Maleic and crotonic acids collect as large crystals inside the condenser, and the liquid con-

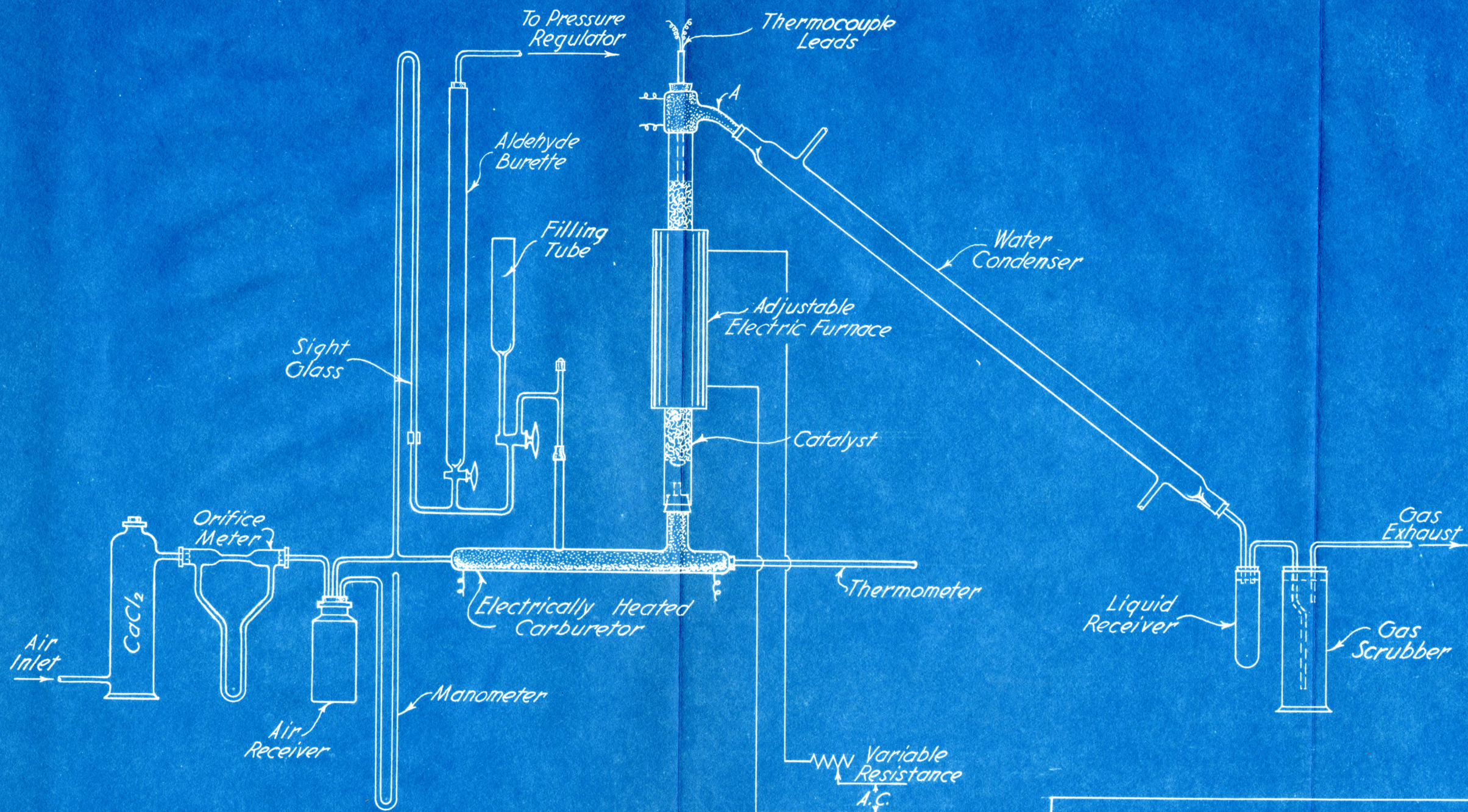


DIAGRAM I
Apparatus for the Catalytic
Vapor-Phase Oxidation
of Crotonaldehyde

densate, which is a solution of crotonic and maleic acids, crotonaldehyde, and water, drains off into the liquid receiver. The exhausting gases, which contain some water vapor and most of the unused crotonaldehyde along with small amounts of crotonic acid, are scrubbed by bubbling through water, and then discharged into the atmosphere.

By means of a connection at point A (not shown), the hot gases from the catalyst were by-passed away from the recovery system for forty-five minutes just before each run was started in order to make sure that equilibrium conditions had been established before the actual taking of data was commenced. At ten-minute intervals during the run, readings were taken and recorded of the rate of air and aldehyde flow, the pressure in the system, the temperature of the gas mixture leaving the carburetor, and the temperature indicated by a thermocouple located in the body of the catalyst.

Because of the intricate construction of the apparatus, a number of features will not seem justified without a more detailed discussion of the reasons for which each was included in the design.

Design of the Apparatus

Preparation of Catalyst. Whatever the true explanation

of contact catalysis may be, it is undoubtedly a surface phenomenon, and, therefore, the structural and thermal characteristics of the catalytic surface are of paramount importance in the reaction (8). Since slight differences in the nature of two catalysts can be responsible for considerable differences in their activities, great pains were taken to use exactly the same method in preparing all catalysts in order to minimize all possible errors from this source.

According to Faith and Keyes (3), the form of the catalyst which has the highest coefficient of heat transfer is most satisfactory. Oxidation will be most rapid at certain active regions, and if the heat evolved is not conducted away from these localized high-temperature spots, the process may be carried to completion instead of stopping at an intermediate point, or the influence of the catalyst may be destroyed by the excessive kinetic activity of its molecules. Furthermore, poor heat-conducting materials might introduce great errors in the determination of catalyst temperatures.

In addition to being of a uniform structure and of a high thermal conductivity, the catalyst must be rigid, relatively porous, and if a carrier is used to support the catalytic material proper, it should have no effect on the reaction lest misleading information be obtained. An excel-

lent catalyst which meets all the above requirements very well can be prepared in the following manner:

Short strips of aluminum turnings are rolled into uniform little balls about three millimeters in diameter. This material is cleaned in a strong solution of oxalic acid and then thoroughly rinsed in distilled water. The clean aluminum is placed in a beaker and covered with five-thirds of its volume of distilled water. The ingredients which are to serve as the catalysts, i. e., the vanadium or molybdenum oxides, are then added, and the whole mixture vigorously stirred while being evaporated rapidly to dryness. When cool, the little pellets are placed in the catalyst tube and heated at from 250 to 300 degrees Centigrade in a strong current of dry air until a uniform color has been produced and no odors can be detected in the exhaust air. Care should be taken in filling the catalyst tube not to leave any open spaces or gaps in the catalyst which might produce channeling.

Thermometry. In addition to its influence on the activity of the catalytic surfaces, the temperature has a very pronounced effect on the rate of the reaction. The quantitative relation of Arrhenius,

$$\frac{d \ln k}{d T} = \frac{E_2}{RT}$$

in which k is the specific reaction rate, E is the so-called "energy of activation," R is the gas constant, and T is the absolute temperature, shows that the speed of a reaction increases with tremendous rapidity as the temperature rises (9). Thus, since the temperature works hand in hand with the catalyst in promoting the oxidation process, and also since the catalyst temperature can vary more than 100 degrees for each centimeter of length, the need for accuracy in determining the true catalyst temperature cannot be over-emphasized.

The usual method of measuring the catalyst temperature is to place a thermometer bulb in the most active region of the catalyst and call the temperature at this point the catalyst temperature. This method is entirely unsatisfactory for the purpose at hand, for not only does the temperature vary a great deal from point to point along the catalyst, but also the point of maximum temperature shifts up and down the catalyst according to different operating conditions.

An adjustable thermometer, by means of which the temperature along the entire length of the catalyst might be explored, was, therefore, devised. A chromel-alumel thermocouple was constructed and accurately calibrated by comparison at several known temperatures. A small pyrex glass tube

just large enough to accommodate the thermojunction and its leads was closed and enlarged at one end so as to support a small aluminum gauze disc which in turn was to hold up the catalytic material. This tube was placed inside the large catalyst tube (see Diagram I) and the catalyst packed in around it. A second aluminum gauze disc held tight the upper end of the catalyst. All was held firmly in place by a rubber stopper through which the small pyrex tube was allowed to project about five centimeters. The thermocouple could thus be moved freely up and down the catalyst and the temperature at any point easily and accurately obtained.

Carburation. Exact control and accurate measurement of aldehyde and air flows are obviously indispensable in an investigation of this sort. Of the several methods of carburation, the most popular is a design in which a primary current of air is allowed to bubble through the liquid until saturation is obtained. The vapor-laden primary air then joins a current of secondary air which is regulated so as to produce the correct ratio of organic vapors and air (2) (3). This method is quite satisfactory where highly volatile alcohols are being vaporized, although close regulation of the alcohol-air ratio is difficult, and measuring the quantity of liquid consumed is rather inconvenient. But due to the fact that crotonaldehyde is easily oxidized by intimate con-

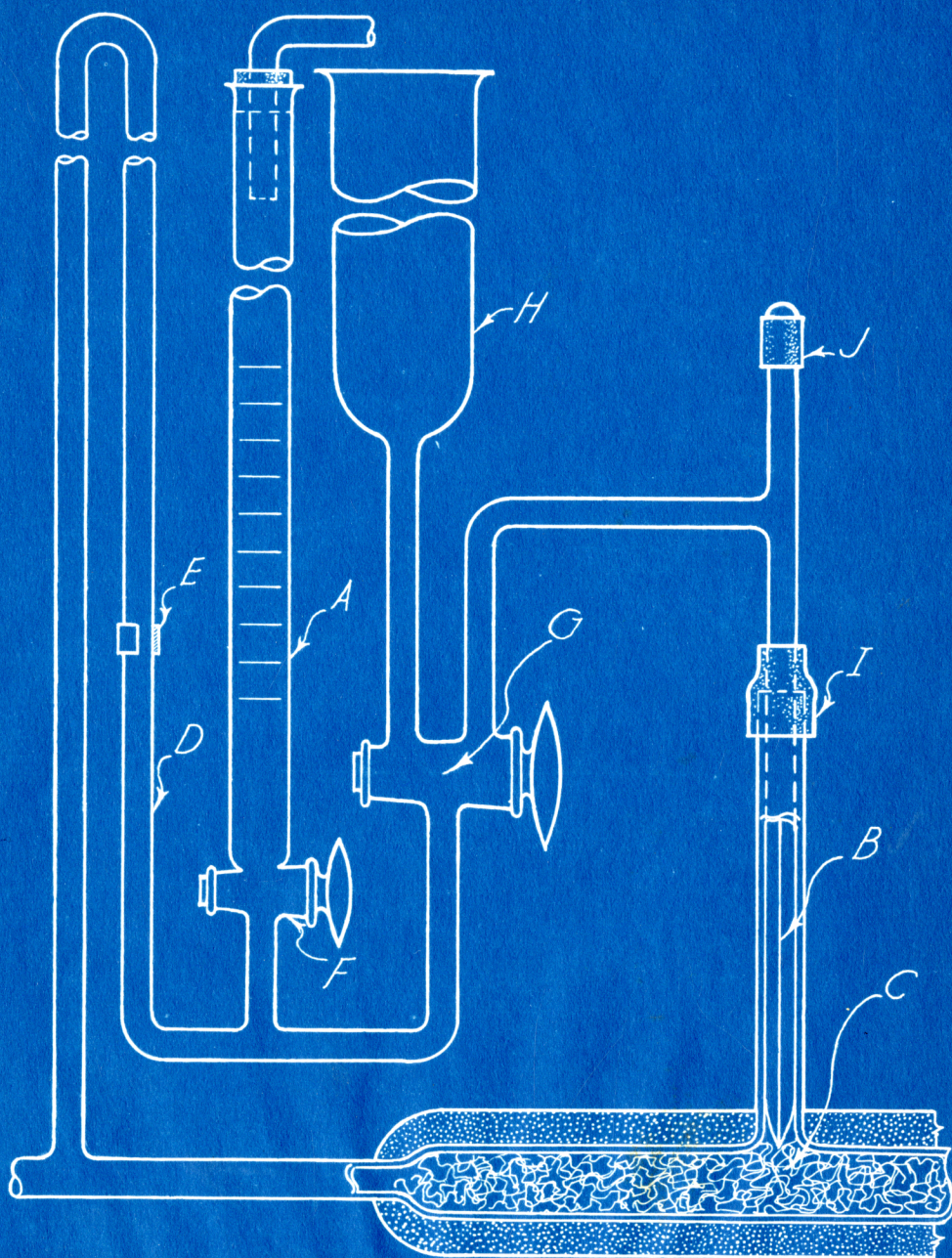


DIAGRAM II
Design of Carburetor
for Vapor-Phase Oxidation
of Crotonaldehyde

tact with air to crotonic acid, which is very soluble in crotonaldehyde, many serious errors would be introduced if the bubble method of carburetion were used.

The type of carburetor which was finally developed for this work is shown on Diagram II. It is essentially a device for maintaining a constant fluid pressure above a small capillary tube through which the aldehyde flows. The burette, A, serves as a reservoir for the crotonaldehyde and also provides an accurate and convenient means of measuring the volume of aldehyde consumed over a whole run or for short intervals of time while the run is in progress. The burette is connected by glass tubing to a small capillary tube, B, from which the aldehyde slowly flows onto the aluminum baffling of the electric air preheater, C. The rate of aldehyde flow will be determined by the diameter of the capillary tube and the fluid head above it. The former is, of course, fixed by the original construction of the apparatus, and so the final control is obtained by regulating the air pressure in the aldehyde burette. As an indicator of the difference in pressure above and below the orifice, a small glass tube, D, is connected as shown in the diagram to the air inlet just above the heater. A movable marker, E, serves as an index and thus assists in keeping the correct pressure in the burette. This marker was also of a certain

width such that if the aldehyde burette stopcock, F, were closed, the time in which the meniscus dropped past the marker would be a fair indication of the rate of aldehyde flow. The aldehyde burette could be easily refilled by properly setting the two-way stopcock, G, filling the receptacle, H, and then applying a slight suction to the aldehyde burette. Assembling and dismantling the carburetor is facilitated by use of the rubber collar, I, which makes it possible to remove the capillary tube from the larger tube in which it is ordinarily incased. A removable cap, J, on the top of the capillary tube provides an opening through which the capillary and orifice may be cleaned without disturbing the rest of the apparatus.

By this type of carburetor, it is possible to maintain a very close regulation of the rate of aldehyde flow, thereby producing any aldehyde-air ratio which might be desired. Furthermore, all of the aldehyde which leaves the burette is carried on into the catalyst tube, although some of it may be in the form of crotonic acid vapors which have been formed by oxidation with the hot air in the heater.

Recovery of Product. Recovering the product is very simple. At the end of a run, the flow of aldehyde and air is stopped. Then, by loosening the condenser clamps, it is possible to slip the condenser off and away from the rubber

stopper by which it is connected to the outlet of the catalyst tube. It is then an easy matter to fill the condenser and liquid receiver by pouring distilled water into the upper end of the condenser until all the air has been displaced. A few minutes' wait will permit all the solid material to dissolve away from the glass of the condenser, and the strong solution thus formed can be drained out into a volumetric flask. Several washings with fresh water will remove the last traces of acid from the apparatus, the wash water being combined with original solution in the volumetric flask. If necessary, more water is added to the flask until a volume of 500 milliliters has been made up. If the yields are very small, it is sometimes best to make the solution up to only 250 milliliters. This final solution can then be titrated with a standardized base in the presence of a suitable indicator, and the quantity of yield thereby determined.

Determination of Yields

The 500-millimeter solution, which contains all the crotonic and maleic acid formed during the run, is then titrated in 25-millimeter samples with N/10 sodium hydroxide, methyl orange and phenolphthalein being used as indicators. An investigation of the ionization constants of crotonic

acid, maleic acid, and sodium hydroxide justifies the use of methyl orange to indicate the neutralization of the first acid group on the maleic acid, and the use of phenolphthalein to show the point at which all the crotonic and maleic acid has been neutralized. The titration of a sample to the methyl orange end point will, then, indicate the number of moles of maleic acid. The titration of a second sample to the phenolphthalein end point will give the combined total of maleic and crotonic acids. If the methyl orange titration is doubled and then subtracted from the phenolphthalein titration, the difference will be the number of milliliters of standard base which were used up in neutralizing the crotonic acid.

Due to the fact that unused crotonaldehyde will impart a yellowish tint to the acid solution, which may be confusing in the methyl orange titration, a specially prepared color blank should be used. The phenolphthalein titration is first made. Then a little more than half this amount of standard base is added to a sample of acid and the proper amount of methyl orange indicator dropped in. As the methyl orange titration can never be more than half the phenolphthalein titration, the addition of this amount of base will insure that all of the first acid group on the maleic acid has been neutralized. The resulting control blank can

then be used as a standard for comparison in the regular methyl orange titration.

RESULTS

In accord with the purposes of this investigation, a series of runs was made in which catalysts consisting of vanadium oxide alone, molybdenum oxide alone, a mixture of vanadium and molybdenum oxides, and, finally, a mixture of vanadium, molybdenum, and titanium oxides was used. The conditions of the runs were varied so that the effect of different catalyst temperatures, different aldehyde-air ratios, and different gas velocities might be studied in addition to the effect of the catalyst itself.

The results of these runs are given in the tables which follow. The composition of the catalyst used in each series of runs is also included. Space velocities are given in liters of reactants per liter of catalyst per second. Representative curves showing the average catalyst temperatures during each series of runs appear in the accompanying figures.

Table 1. Vanadium Oxide Catalyst

30 ml aluminum carrier material
50 ml distilled water
6.0 grams ammonium vanadate

Run Number	Space Velocity	Moles Ald. per Mole of Air	Furnace Position	% Conversion to Acid
1	1.666	.00487	Center	17.31
2	2.812	.00686	Top	15.05
3	1.666	.00312	Center	24.60
4	2.312	.00265	Center	28.65

Catalyst temperatures are shown in Figure 1.

Table 2. Molybdenum Oxide Catalyst

30 ml aluminum carrier material
 50 ml distilled water
 6.5 grams molybdic acid

Run Number	Space Velocity	Moles Ald. per Mole of Air	Furnace Position	% Conversion to Acid
1	1.666	.00503	Center	9.34
2	2.812	.00546	Center	None
3	1.666	.00933	Center	5.76
4	2.812	.00628	Center	None
5	1.666	.00551	Center	2.61

Catalyst temperatures are shown in Figure 2.

Note: In this series of runs, the apparatus was lined with a dark brown tar-like material which was only slightly soluble in water, but quite soluble in alcohol.

Table 3. Vanadium and Molybdenum Oxide Catalyst

30 ml aluminum carrier material
 50 ml distilled water
 5.0 grams ammonium vanadate
 2.5 grams molybdic acid

Run Number	Space Velocity	Moles Ald. per Mole of Air	Furnace Position	% Conversion to Acid
1	1.666	.007210	Top	27.50
2	1.666	.003505	Center	25.65
3	1.666	.003328	Bottom	23.45
4	1.666	.002985	Center	28.15
5	1.666	.004535	Top	25.48
6	1.666	.004940	Bottom	27.00
7	1.666	.004550	Top	24.90

Catalyst temperatures are shown in Figure 3.

Fig. 1. Showing the temperature at various points along the catalyst during typical runs with vanadium oxide as a catalyst.

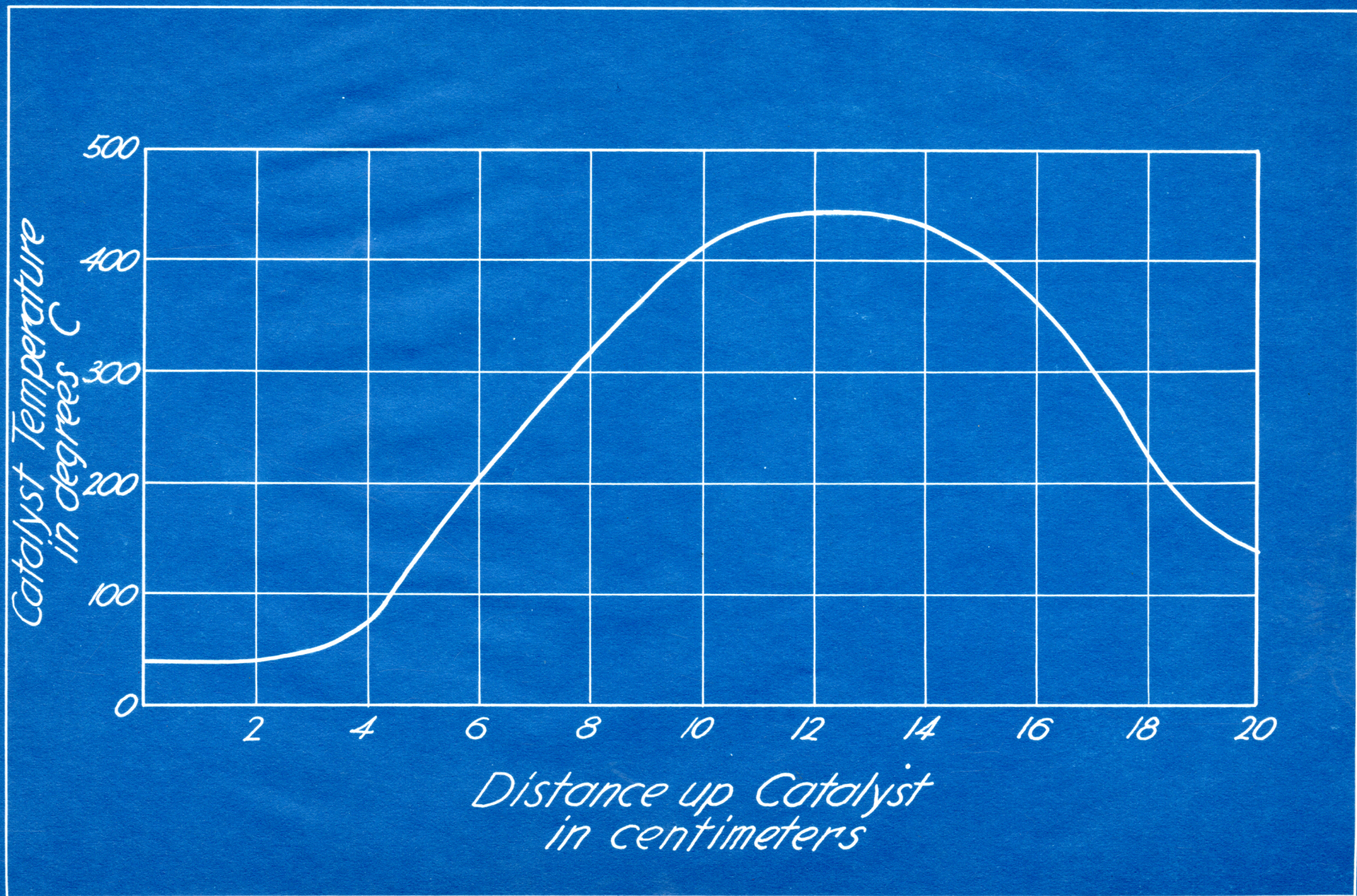


Fig. 1.

Fig. 2. Showing the temperature at various points along the catalyst during typical runs with molybdenum oxide as a catalyst.

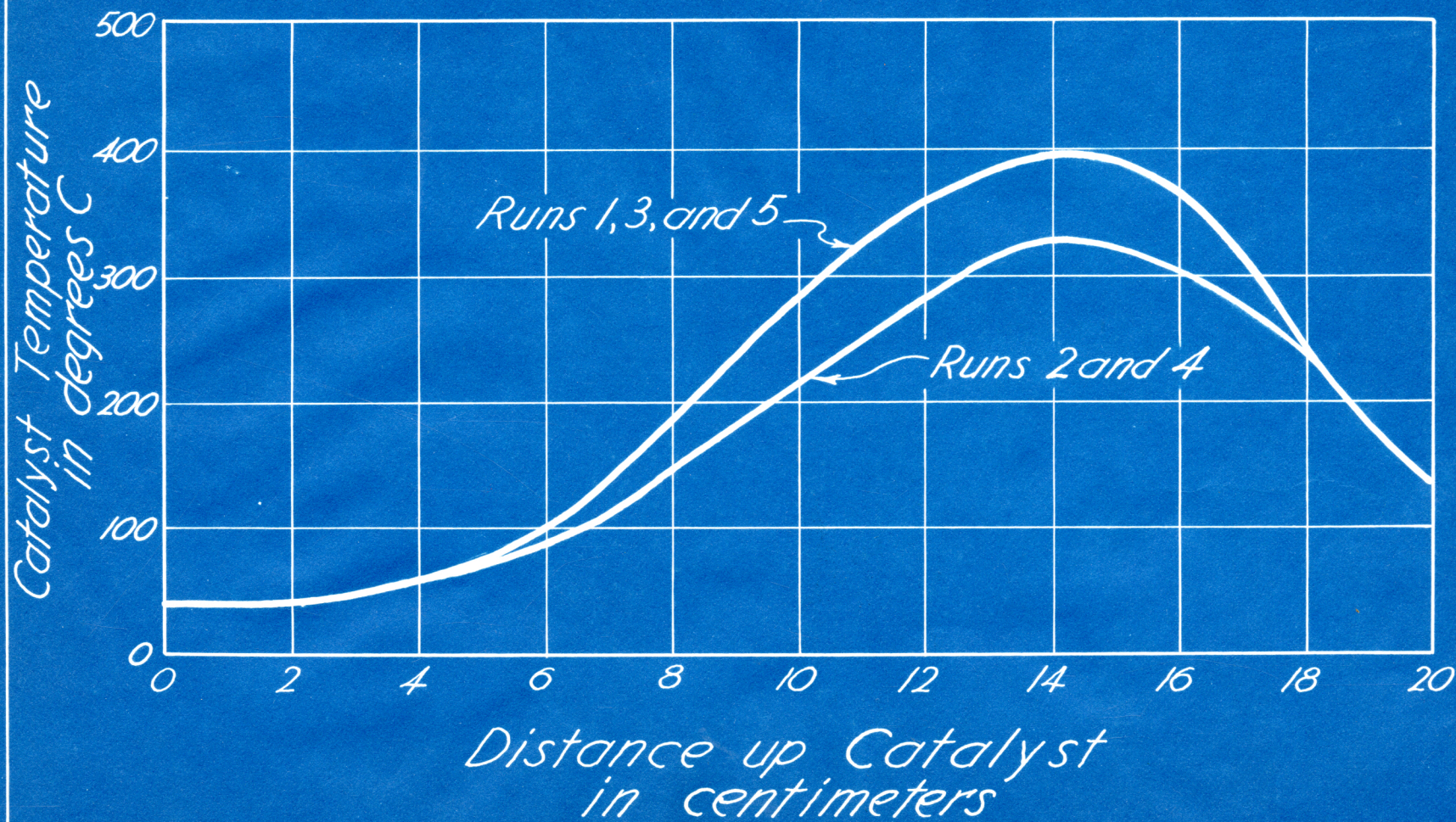


Fig. 2.

Fig. 3. Showing the temperature at various points along the catalyst during typical runs with a catalyst composed of a mixture of vanadium and molybdenum oxides.

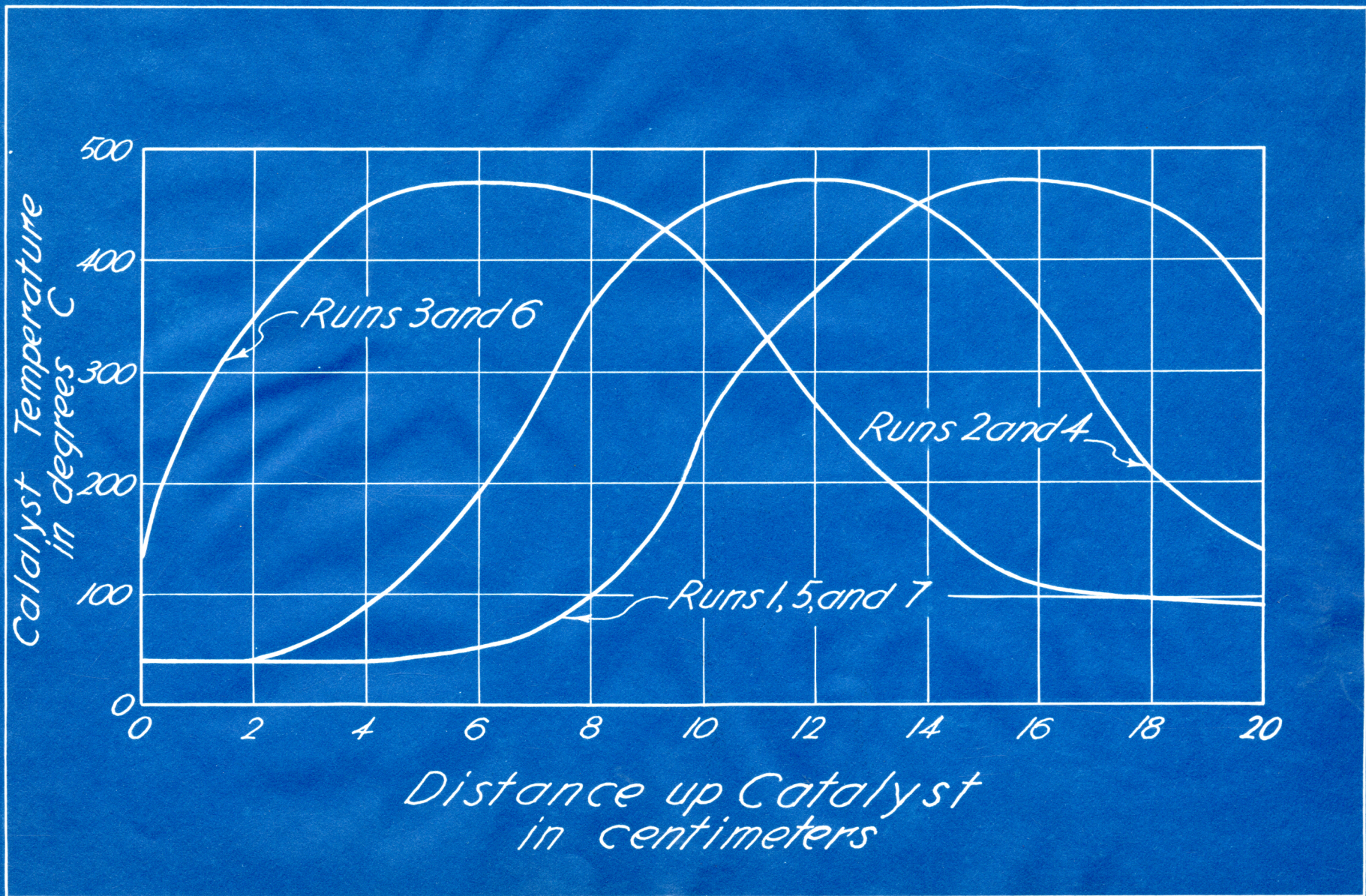


Fig. 3.

Fig. 4. Showing the temperature at various points along the catalyst during typical runs with a catalyst composed of a mixture of vanadium, molybdenum, and titanium oxides.

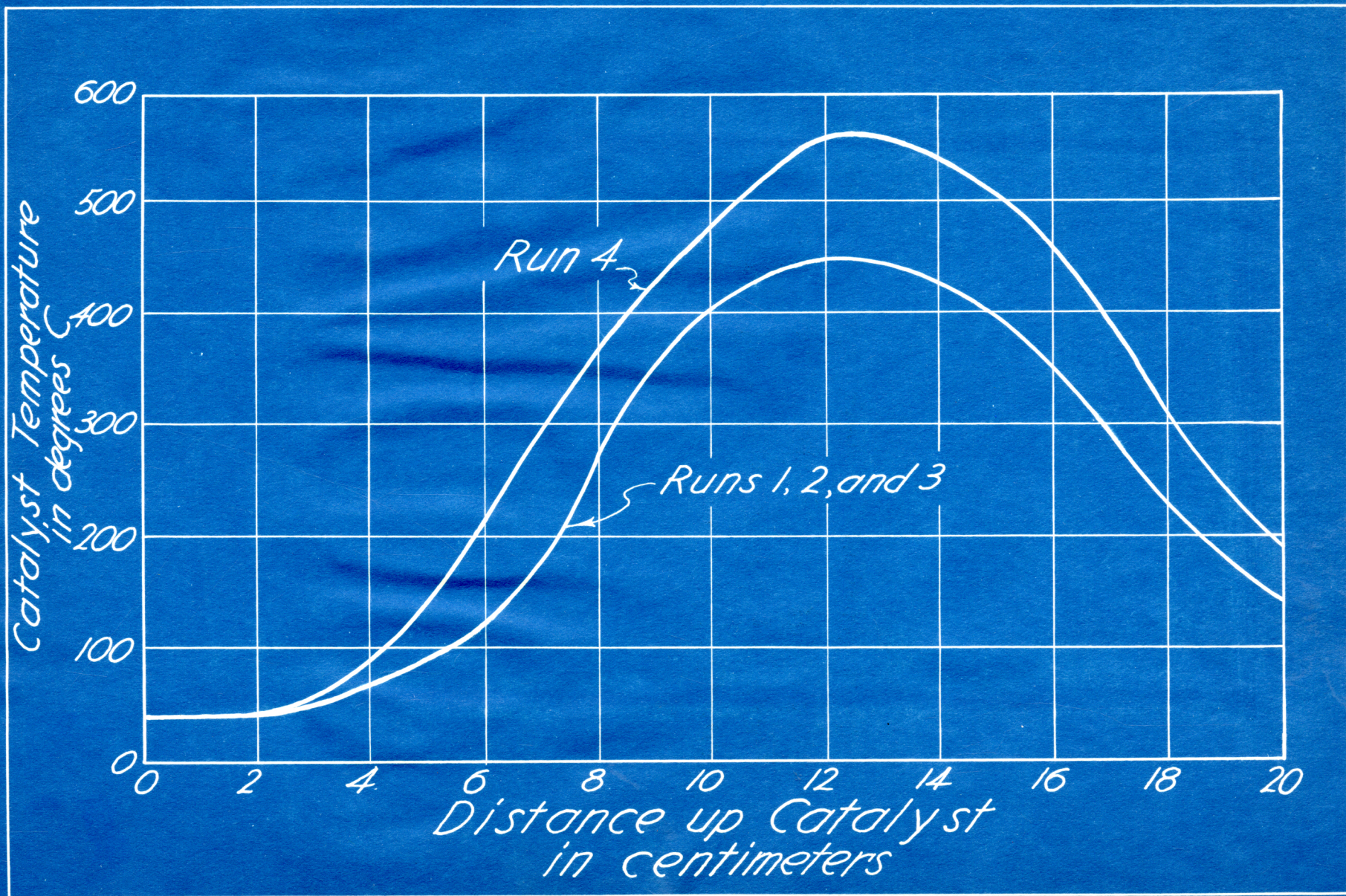


Fig. 4.

Table 4. Vanadium, Molybdenum, and Titanium
Oxide Catalyst

30 ml aluminum carrier material
50 ml distilled water
5.0 grams ammonium vanadate
2.5 grams molybdic acid
1.0 gram titanium oxide
1.5 grams oxalic acid

Run Number	Space Velocity	Moles Ald. per Mole of Air	Furnace Position	% Conversion to Acid
1	1.666	.005430	Center	18.55
2	1.666	.004500	Center	17.24
3	2.312	.002645	Center	28.00
4	2.312	.003005	Center	27.90

Catalyst temperatures are shown in Figure 4.

DISCUSSION OF RESULTS

A thorough treatment of any one of the four major projects outlined above would necessitate the making of far more runs than were possible altogether in this preliminary investigation of the general mechanics of the reaction. Nevertheless, valuable information concerning the behavior of the various catalysts studied has been obtained, and a definite correlation between the completeness of the reaction and certain physical dimensions of the system has been observed.

The Effect of the Catalyst

The adsorption theory of contact analysis (7) suggests that adsorbed reactants are made more active by the increase in concentration, by a chemical affinity between reactants and catalyst through the use of unsaturated catalyst valences, by molecular orientation at the catalytic surfaces, or by some alteration in the nature of molecular impacts so that the number of active impacts is greatly increased.

In the light of the adsorption theory, a very logical explanation for the crotonaldehyde oxidation can be formulated. The metallic oxide catalyst evidently possesses a pronounced affinity either for the double bond alone or for the crotonic acid group, $-\text{CH}:\text{CH}-\text{COOH}$. This affinity may manifest itself as a form of preferential adsorption, or the formation of an intermediate complex compound in which the double bond or the crotonic acid group is held by unsaturated catalyst valences. A molecule of crotonic acid should have distinct polar characteristics, and its structure indicates that it may be somewhat oblong in shape. It seems reasonable, therefore, to imagine that the comparatively slender polar molecules of crotonic acid are carried by convection currents or diffusion into the proximity of an ac-

tive catalytic region where, under the influence of adsorptive, gravitational, or electrical forces, they are caused to assume more or less restricted relationships to the structural and energy schemes of the catalyst. The adsorbed molecules need not be held in a definite position as is characteristic of the molecules in true compounds, but could be restricted to more or less confined positions with respect to the catalyst and still have considerable vibratory motion of a translatory nature. The crotonic acid molecules would be oriented in such a way as to protect the double bond and to expose the methyl group to active impact with oxygen molecules. An oxidation of the methyl group while the molecule was being influenced by the catalyst could easily destroy that property, polar or otherwise, by means of which the catalyst held onto the organic molecule. The maleic acid molecule, no longer held fast by the catalyst, could then evaporate a way from the catalytic surface.

It may seem that in the preceding discussion undue importance was given to crotonic acid in the reaction. This was not done without reason, however. Since crotonaldehyde is so easily oxidized to crotonic acid when exposed to air even at room temperatures, it seems doubtful that much crotonaldehyde reaches the hot catalyst surfaces before oxidation of the aldehyde group has taken place. Furthermore,

except where molybdenum oxide was used alone as a catalyst, the yields of crotonic acid were negligibly small in comparison to the amounts of maleic acid. This would indicate that nearly all crotonic acid formed during the process was oxidized to maleic acid before it left the catalyst tube. According to Drossbach (2), crotonic acid may be used alone and still produce good yields of maleic acid.

Vanadium oxide is apparently the most important catalyst in promoting the reaction. Molybdenum oxide, when used alone, is evidently capable only of producing some sort of condensation among the aldehyde molecules. But the best yields were obtained when molybdenum oxide was used in conjunction with vanadium in preparing the catalyst. Catalyst temperatures were considerably higher in the runs with the mixed catalyst than they were when molybdenum oxide was used alone, and this could well account for a higher concentration of crotonic acid in the reacting mixture, particularly at the catalytic surfaces.

Since titanium is next adjacent to vanadium in the periodic table, its oxide might well be expected to catalyze the reaction to a certain extent. The effect of titanium oxide alone was not investigated, and when it was used with vanadium and molybdenum oxides, no decisive results were noticed.

The Influence of the Reaction Temperature

It has been pointed out that the temperature has a marked effect on the rate of reaction from the standpoint of the reactants themselves. No quantitative relation between the completeness of the reaction and the temperature can be made on the basis of the limited number of runs made. Yields were better when the catalyst heater was located at the bottom of the catalyst tube and the region of maximum temperature extended over almost half the length of the catalyst than they were when the furnace was at the top of the tube and the high temperature extended over only a few centimeters. (See Fig. 3.). In general, it may be said that yields were better at higher average catalyst temperatures, although elevated temperatures affect the catalyst and its activity so that the temperature can not be raised much above 550 degrees without reducing the yields and damaging the catalyst.

The Significance of Concentrations in the Reacting Mixture

A definite correlation was found to exist between the aldehyde-air ratio and the per cent of aldehyde converted to acid when vanadium oxide was used alone as a catalyst. The

curve of this relation, which is shown in Figure 5, indicates that the efficiency of conversion increases with an increase in excess air, the maximum conversion found being 28.65 per cent with an aldehyde-air ratio of .00265 moles of aldehyde per mole of air. The original design of the apparatus would not permit making runs with a smaller ratio of aldehyde to air, but the point of maximum conversion will probably lie somewhere between a ratio of .0025 and zero.

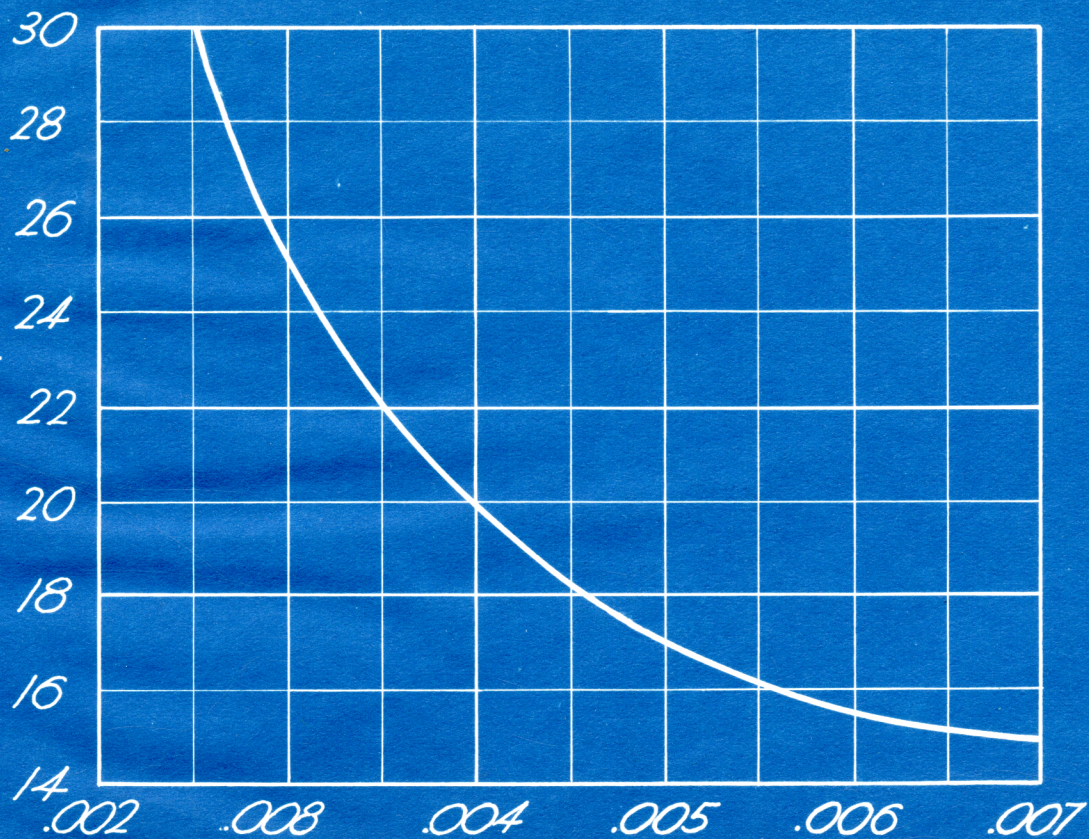
It seems that, regardless of the other conditions of the system, the yields were higher at lower aldehyde-air ratios, but a much more extensive investigation of the process must be made before a thorough discussion of this relation will be possible.

The Significance of Space Velocity

The rate at which the gases pass over the catalyst has no great effect on the efficiency of conversion within the limited range of conditions studied. However, obtaining the exact relation between the efficiency of conversion and the space velocity is probably the most difficult problem of all confronting an investigator of a catalytic vapor-phase process, and it also presents the greatest source of error in the investigation. When the space velocity is changed, all the other variables within the system are also

Fig. 5. Showing the percent conversion of crotonaldehyde to maleic acid with respect to the concentration of crotonaldehyde in the reacting mixture.

*Percent Conversion
of Aldehyde to Acid*



Mols Aldehyde per Mol Air

Fig. 5.

materially altered at the same time. The amount of material oxidized per unit time is changed, and this, in turn, changes the amount of heat liberated at the catalytic surfaces. The manner in which this heat of reaction is dissipated is also greatly altered; the ratio of heat leaving in the gases to that being conducted away through the catalyst can be expected to change a great deal with a corresponding effect on the oxidation reaction. Furthermore, convection currents and rates of gaseous diffusion will be vastly different at different gas velocities, and consequent effects on the rate of the reaction, to say nothing of the accuracy of temperature measurement, are obviously to be encountered. A very thorough study of the process with this one relation as the primary objective must be made before the final solution of this problem can be reached.

SUMMARY AND CONCLUSIONS

A laboratory apparatus of simple construction has been developed for the catalytic vapor-phase oxidation of unsaturated aldehydes.

It has been found that crotonaldehyde can be most efficiently oxidized to maleic acid by the use of catalysts in which vanadium oxide is the primary constituent.

Molybdenum oxide promotes the oxidation of crotonaldehyde to maleic acid when used in conjunction with vanadium oxide, but it produces only tarry materials and no maleic acid when used alone.

Oxidation to maleic acid is evidently greatest when high catalyst temperatures, moderate space velocities, and low aldehyde-air ratios are used.

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